METALS & RADIONUCLIDES FOUND AT CONTAMINATED SITES

This primer looks at ways microbial processes can be used to help remediate soils, sediments, and groundwater contaminated with metals and radionuclides. Section II provided a general introduction to bioremediation and an overview of the various bioremediation technologies. In this section, we describe several of the metals and radionuclides of most concern at many Department of Energy sites. These contaminants are the radionuclides cesium, plutonium, strontium, technetium, and uranium; and the metals chromium, lead, and mercury. Figure 3.1 illustrates their frequency of occurrence in groundwater, and in soils and sediments at DOE facilities.

These metals and radionuclides are all waste products of nuclear fuel production, nuclear research, and nuclear reactor operations at DOE facilities. Many of the metals are also found in industrial and/or agricultural waste products. This section looks at how their transport properties and toxicity are influenced by their oxidation states,[1] solubility, and sorption processes. Transport and toxicity are both affected by contaminant form. One form or species of a metal or radionuclide may be harmless, while another can be extremely toxic. In addition, one species may be extremely mobile because it is water soluble, while another is immobile because it is in a solid phase or adsorbed to a mineral surface.

RADIONUCLIDES

Radionuclides in the environment can be present in many forms, depending on the nature of the surrounding environment. They form complexes with natural organic ligands such as humic substances. The solubility of these complexes varies with the pH of the natural aquifers. For example, compounds with hydroxides are common at high pHs.

Radionuclides also can form complexes with inorganic materials such as carbonate and sulfate. Some radionuclides are associated with colloids. At DOE sites, radionuclides such as uranium, plutonium, and strontium were found in some cases to be disposed of with organic substances such as organic acids, complexing agents (such as EDTA), and solvents, all of
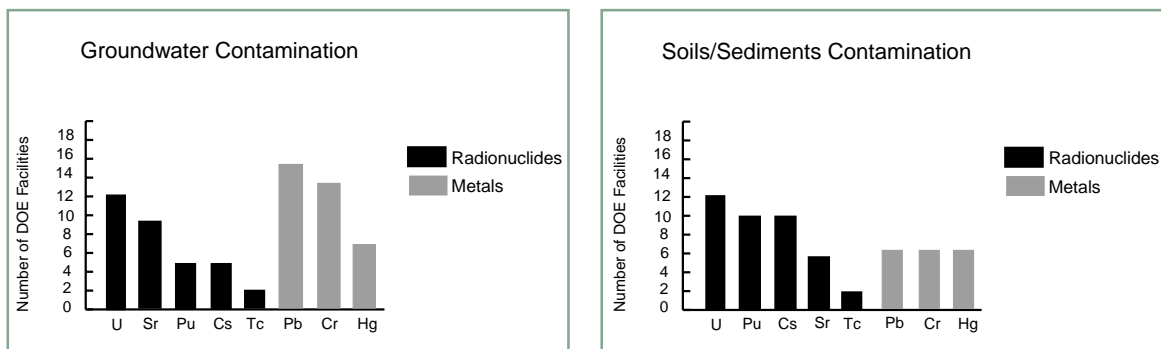

Figure 3.1. **Frequency of occurrence of selected metals and radionuclides in groundwater and soils/sediments at DOE facilities (adapted from Riley et al., 1992).**

1. See the feature "Opposites Attract: Valences, Bonds, and Redox Reactions" on page 23.

which can influence radionuclide geochemical behavior and subsurface transport.

Uranium and strontium have been reported in groundwater at more than 50 percent of DOE facilities, and along with tritium are the most frequent radioactive constituents in DOE groundwater. In DOE soil and sediments, uranium, plutonium, and cesium have been cited as the most common radioactive waste components (Figure 3.1).

Cesium (Cs)

Cesium is a relatively rare, silvery white metal, found in the Earth's crust. Cesium has only one naturally occurring isotope — 133. However, 20 radioactive isotopes have been created, with masses ranging from 123 to 144. The most hazardous and most frequently identified is cesium-137, which has a 30-year half-life.

Cesium-137 is a primary constituent of stored nuclear waste. Large quantities of cesium-137, along with strontium-90, were produced during the nuclear fuel cycle, specifically during the generation of plutonium and enrichment of uranium for use in nuclear weapons. When the fissile weapons materials were then extracted from the fuel rods and processed as hazardous waste, the cesium and strontium were also extracted and processed, and the contaminants stored in waste storage tanks on DOE lands.

Cesium-137 and strontium-90 have been found in large quantities in fallout from the 1986 accident at Chernobyl in Ukraine. Because of cesium's

Figure 3.2. Plutonium in +3 to +7 oxidation states in colored solution, from left to right: Pu(III), Pu(IV), Pu(V), Pu(VI), and Pu(VII).

similarity in chemical properties to potassium, Cs-137 is taken into the body in the same manner, and can result in whole-body radiation. In addition, the beta particles it emits are particularly toxic to bone marrow.

The cesium ion has only one oxidation state: +1. It gives up its electron very easily, forming ionic bonds with nearly all the inorganic and organic anions. Cesium easily loses electrons when struck by light, so it is used extensively in photoelectric cells and television cameras to form electronic images. The cesium-137 isotope is also useful in medical and industrial radiology. Cesium hydroxide (CsOH) is the strongest base known. In soils and sediments, cesium is known to sorb strongly to clays.

Plutonium (Pu)

Plutonium is a silvery metal that takes on a yellow tarnish in air. It is the second of the artificially produced transuranic elements (neptunium being the first). Fifteen isotopes exist, and all are radioactive poisons because of their high rate of alpha emissions and their absorption to bone marrow. Permitted levels of exposure to plutonium are the lowest of any element.

The first isotope discovered was Pu-238 (half-life of 86 years), which was produced in 1940 by deuteron bombardment of uranium in an accelerator. The most important isotope is Pu-239, with a half-life of 24,100 years, which is produced in extensive quantities in nuclear reactors from natural uranium.

Plutonium has five oxidation states (+3, +4, +5, +6, and +7). The more insoluble form of plutonium is the Pu(IV) polymer, a hydrous plutonium oxide. However, in groundwater, the presence of complexing inorganic or organic species strongly influences the solubility of Pu(IV). For example, EDTA, a contaminant often found with actinide waste, is known to enhance solubility of Pu(IV), even in the polymer. Plutonium can also be present in groundwater as a number of other compounds, including plutonium carbonates, plutonium hydroxides, and plutonium sulfates. In anoxic water, water-soluble plutonium occurs as the Pu(III) and Pu(IV) species, whereas in oxygenated waters, Pu(IV), Pu(V), and Pu(VI) may coexist. Pu(V) is known to predominate in seawater and oxygenated lake water.

Strontium (Sr)

Strontium was first found in strontianite ($SrCO_3$), a carbonate mineral. Its other natural ore is celestite ($SrCO_4$). It is an alkaloid metal with one oxidation state: +2. Chemically, strontium is similar to calcium and barium.

The four naturally occurring isotopes are: Sr-88 (82.56%), Sr-86 (9.86%), Sr-87 (7.02%), and Sr-84 (0.56%). Approximately 16 artificial radioisotopes have been produced by nuclear reactions, of which the longest lived and best known is Sr-90 (with an approximate 28-year half-life).

Along with cesium-137, strontium-90 is produced in large quantities during the fission process, so it exists in high concentrations in stored nuclear waste. It is also considered the most dangerous constituent of radioactive fallout (see cesium, above). Because it is chemically similar to calcium, strontium-90 can replace some of the calcium in foods and ultimately become concentrated in bones and teeth, where it continues ejecting ions that cause radiation injury.

Technetium (Tc)

Technetium was the first artificially produced element. The isotope technetium-97 (with a 2.6-million-year half-life) was discovered in 1937 in a sample of molybdenum that had been bombarded by deuterons. Technetium is a silvery-gray metal that tarnishes slowly in moist air. Nineteen Tc isotopes are now known, with atomic masses ranging from 90 to 108. All of them are radioactive.

Technetium can assume all oxidation states from +7 to 0. However, oxidation states +4, +5, +6, and +7 have the strongest potential to exist in the environment, with Tc(VII) and Tc(IV) dominating. The Tc(VII) pertechnetate ion (TcO_4^-) is highly stable in water under oxic conditions and may represent the species that is most mobile in groundwaters under these conditions. Less soluble sulfide, carbonate, and oxide forms of Tc(IV) represent the most dominant species under anaerobic conditions.

Technetium-99 (with a 212,000-year half-life) is produced in kilogram quantities as a fission product in nuclear reactors. It is derived from uranium and plutonium fission, and is used to absorb slow neutrons in reactors. It may enter the environment via several avenues, such as through the separation and enrichment of uranium, and thus is present in stored wastes at a number of DOE sites, including Hanford, Paducah, and Portsmouth. These radionuclide wastes, originally stored in lagoons and burial pits, leaked into the subsurface and formed plumes in the sand aquifers below the vadose zone. The Tc-99 in these plumes is believed to be in the form of TcO_4^-. Pertechnetate can be mobile in groundwaters and biologically available, and thus constitutes a significant part of the potential radioactive dose to humans at these sites. This factor, coupled with the long half-life of Tc-99, makes the presence of this radioisotope a great concern.

Technetium-99m, not to be confused with Tc-99, has a short half-life of just over 6 hours. It is an important tracer radioisotope in nuclear medicine.

Uranium (U)

Uranium, with an atomic number of 92, is the heaviest known natural element. It is dense, hard, metallic, and silvery white. Uranium occurs in a number of minerals, including carnotite and uraninite, a dense black variety of which is called pitchblende. Uranium is not all that rare, being more plentiful in the Earth's crust than mercury and silver.

Uranium has four oxidation states: +3, +4, +5, and +6. Uranium(VI) exists in a soluble state and is very mobile in groundwater. Uranium(IV) can be stable in reducing conditions and is highly insoluble, and as particulate matter can be inhaled into the lungs. The ions in the +3 and +5 states are not as stable. Weathering of rocks converts uranium to the +6 state, where it forms the uranyl ion (UO_2^{2+}). Most uranyl compounds tend to be soluble in groundwater, although the phosphates are quite insoluble. When uranyl ions encounter a reducing agent such as organic matter, U(IV) is precipitated (separated from solution) as uraninite and coffinite.

All uranium isotopes are radioactive. In its natural state uranium consists of a mixture of U-238 (99.27%), U-235 (0.72%), and U-234 (0.006%), with half lives of 4.5 billion, 7.13 million, and 247,000 years, respectively.

Natural uranium is used in the generation of nuclear fuel, specifically in converter and breeder reactors. Uranium-235 is one of the two fissile materials used for the production of nuclear weapons, and in some nuclear reactors as a source of energy. The other is Pu-239, which is virtually nonexistent in nature and is made by bombarding U-238 with neutrons in a nuclear reactor. Because of its importance in the fission process, uranium is found in large quantities in stored nuclear waste.

The ionizing radiation from uranium (as well as other radioactive elements) can break chemical bonds, thereby destroying or damaging living cells. The most common routes of uranium contamination are through handling, ingesting, and inhaling. Inhaling and ingesting increase the risk of lung and bone cancer. Uranium is also chemically toxic at high concentrations and can cause damage to internal organs, particularly the kidneys. Uranium may also affect reproductive organs and the fetus, and may increase the risk of leukemia and soft tissue cancers.

Uranium mining to obtain yellowcake is a major source of contamination by uranium decay products. Yellowcake is a yellow or brown uranium oxide powder that is processed to obtain uranium dioxide (UO_2) and uranium metal for use in reactors and nuclear weapons production. Conventional mining techniques generate a substantial amount of mill tailings, which are in the form of thorium-230 and radium-226. These waste products have a half-life of about 75,000 years and 1,600 years, respectively. They can leach into groundwater, and water samples near tailing piles have shown levels of some contaminants to be hundreds of times the government's acceptable level for drinking water. In addition, miners at these sites have died of lung cancers, which can be linked to inhaling uranium decay products.

Enrichment is another frequent source of uranium contamination. Enrichment increases the amount of uranium-235 in natural uranium for use in reactors. Uranium hexafluoride (UF_6), an interim product of the enrichment process, contains the soluble U(VI) ion and is highly radioactive and toxic. It reacts readily with moisture, releasing highly toxic hydrofluoric acid. Enrichment facilities have had a number of accidents involving UF_6.

METALS

Chromium (Cr)

Chromium in its naturally occurring form is found mainly in chromite. The mineral chromite is composed of iron, chromium, and oxygen ($FeCr_2O_4$). It is formed in the deep subsurface, which gives this mineral a stable crystalline structure and a resistance to high temperatures and pressures. Chromium is an essential trace element and has a role in glucose metabolism.[2]
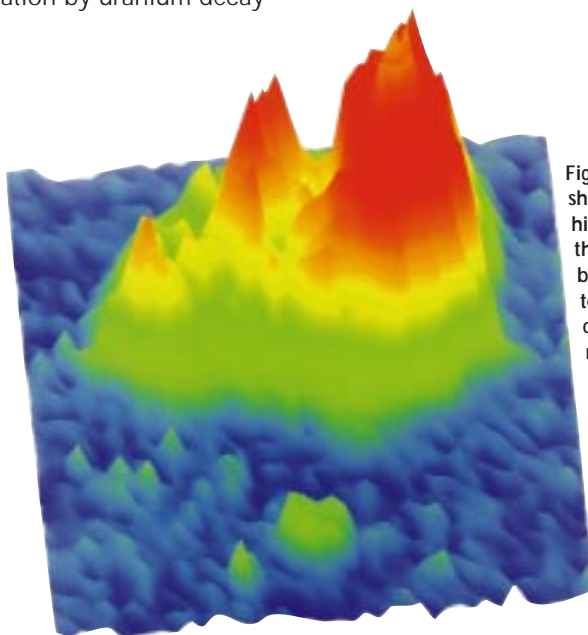
Figure 3.3. This computer image shows that chromium is present in highly localized chemical hot spots in the soil. The color scale ranges from blue, which indicates no Cr present, to red-orange, which indicates a concentration of one picogram per micrometer. The image was generated on the x-ray fluorescence microprobe beamline at Lawrence Berkeley National Laboratory's Advanced Light Source. (Courtesy of Tetsu Tokunaga.)

Chromium is found in three oxidation states (+2, +3, and +6), although in a few stable compounds it also exists in the +5, +4, and +1

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2. To learn more about the chemical and physical properties of chromium and other elements, visit Britannica Online, at http://www.eb.com/ (Encyclopedia Britannica, 1998).

states. The most commonly found oxidation states are +3 and +6, with +6 being the most toxic. Trivalent chromium is an essential nutrient required in sugar and fat metabolism, and in the action of insulin. Hexavalent chromium is toxic and carcinogenic.

Chromium wastes are associated with reactor operations, fuel fabrication, and irradiated fuel processing at DOE facilities, and the toxic and soluble Cr(VI) form is reported in soils and sediments on DOE lands. Chromium(VI) can also enter the environment in effluents from metal plating and through exposure through handling and inhalation, and in industrial or municipal waste treatment plant discharges.

Chromium(VI) is highly soluble; i.e., it can dissolve easily in water and move through the subsurface environment. It has been found to cause throat and lung cancer, and long-term toxic effects may include shortened life span, reproductive problems, and lower fertility.

Chromium(VI) dissolved in groundwater is typically found in the form of CrO_4^{2-} at neutral and high pH. Under acidic conditions it occurs as $HCrO_4^-$. Dissolved Cr(III) occurs as $Cr(OH)_3$ at neutral and alkaline pH, and $Cr(OH)_2^-$ under acidic pH. Other inorganic and organic complexes with Cr(III) also occur. Solubilities of Cr(III) species are generally very low. Chromium(III) is reoxidized to Cr(VI) through redox reactions with MnO_2. Chromium precipitates occur primarily as Cr(III) compounds. Reduction of Cr(VI) to Cr(III) in sediments and groundwater can be due to organic compounds (including natural organic matter), ferrous iron [Fe(II)], and sulfides [S(–II)]. Chromium(III) sorbs strongly onto Fe and Mn oxides, clays, and other mineral surfaces. Chromium(VI) also sorbs onto Mn, and Fe oxides. Biotransformation of Cr(VI) to the less toxic and mobile Cr(III) presents an opportunity for bioremediation of chromium.

Lead (Pb)

Lead has two oxidation states, +2 and

Figure 3.4. Lead is usually found with sulfur in the mineral galena (PbS).

+4, and is toxic in both. It is bluish-white with a bright luster in its elemental state.

Lead(IV) is generally the more soluble ion. PbO_2 is a lead oxide that is soluble in water. Lead(II) is generally insoluble in groundwater. Lead carbonate [$Pb(CO_3)$] and lead sulfate [$Pb(SO_4)$] are insoluble Pb(II) compounds. Lead(II) monoxide (PbO), in the forms of litharge and massicot, is also insoluble in water, but readily dissolves in acid.

Lead wastes are associated with reactor operations and lead ions are found in high concentrations in groundwater at DOE facilities. Lead is also used extensively in industry. Great quantities of lead, both as the metal and as the dioxide, are used in storage batteries. Lead is used in ammunition and in radiation shields. Lead poisoning, also called plumbism, is caused by repeated exposure to the metal, resulting in its accumulation in the body tissues. Lead affects the intestines and central nervous system and causes anemia.

Children are especially susceptible to lead poisoning as the blood–brain barrier has not yet fully developed. Therefore, lead can more easily enter the brain. At lower levels of exposure, children can experience behavioral changes and decreases in intelligence. At high levels, children can suffer severe brain damage and die.

Environmental concern with lead poisoning has resulted in the elimination of lead from gasoline and paint products. Although elemental lead and some lead compounds are not absorbed by human tissue and are, therefore, not toxic, any soluble lead compound is toxic, with toxicity increasing as solubility increases.

Mercury (Hg)

Mercury is the only elemental metal that is liquid at room temperature. Mercury is very volatile, meaning that it can readily vaporize at relatively low temperatures. In its solid form, it is silvery white, slowly tarnishing in

moist air, and freezing into a soft solid like tin at about -39°C (-38.2°F). It alloys with most metals. Mercury's principal ore is the red sulfide, cinnabar (HgS).

Inorganic mercury exists in three oxidation states: 0 (elemental mercury); +1 (mercurous mercury); and +2 (mercuric mercury). Mercury compounds contain either the Hg(I) or Hg(II) ion, although Hg(II) compounds predominate. All three oxidation states are toxic. The most volatile form, metallic Hg(0) vapor, is lipid soluble and readily absorbed via the respiratory tract. Less volatile, water soluble methylmercury (CH_3Hg) is readily absorbed via the gastrointestinal tract, and also by inhalation. Water-soluble Hg(II) is modestly absorbed from the gastrointestinal tract because of its low lipid solubility. In general, mercury is a cumulative toxin, with all forms tending to excrete very slowly once fixed in a tissue.

Common anthropogenic sources of mercury include nuclear fuel production at DOE facilities as part of the uranium purification and isotope separation process (U-235 and U-238), industrial mining, burning of fossil fuels, and pesticides. Sewage treatment facilitates are a widespread source of both inorganic and organic mercury compounds (Hg(0), Hg(II), methylmercuric chloride, and dimethylmercury).

The major form of mercury in the atmosphere is elemental mercury, which is highly volatile. Burning of fossil fuels contributes to this atmospheric contamination. Even though elemental mercury, Hg(0), is the least reactive of the three oxidation states, it is still poisonous because it is readily oxidized to the most reactive form, Hg(II), by both biotic and abiotic processes. This mercuric ion can then enter aquatic environments. Mercury in the form of Hg(II) also enters aquatic environments from industrial and nuclear fuel production wastes, and agricultural runoff waters. These pollutants then settle into river and lake sediments.

The mercuric ion readily adsorbs to these sediments and other particulate matter. Anaerobic sulfate-reducing bacteria, which commonly inhabit sediment, can methylate this ionic mercury, forming methylmercury (CH_3Hg). Because it is both lipid and water soluble, methylmercury readily enters the aquatic food chain. Fish contaminated with methylmercury have been found in freshwater from Japan to the Great Lakes. Methylmercury is about a hundredfold more neurotoxic than ionic mercury [Hg(II)] and can be concentrated a millionfold in fish. Additional methylation by microorganisms produces dimethylmercury (CH_3HgCH_3), which is even more volatile and lipid soluble, but which must be partially demethylated before it can react with tissue proteins.

Although methylmercury is highly toxic, bacteria have evolved genes that convert it to a much less toxic form. Thus, methylmercury is a suitable candidate for bioremediation. Alternative strategies, such as vapor extraction followed by collection of the volatile methylmercury, would require elaborate containment. This would be difficult for dry land decontamination or lake sediment remediation. Demethylating microbes are often found in sediments containing the methylating sulfate-reducing bacteria. Their demethylating activities could be enhanced by several interventions, including but not limited to, amendment with native or non-native demethylating microbes or by phytoremediation.

OPPOSITES ATTRACT:
VALENCES, BONDS, AND REDOX REACTIONS[1]

Atoms bond to achieve stability. Chemical bonds are formed through the giving up, receiving, or sharing of electrons by the outermost region of an atom, called its valence shell. The valence-shell electrons are the least tightly bound to the nucleus and therefore can be removed the most easily.

The oxidation number of an atom is the net charge on an atomic species. And the atom's oxidation state (also known as its valence) is the number of electrons an atom can give up or receive to achieve a bond. The oxidation state of any atom is indicated by a roman numeral following the name of the element. Thus, iron(III), or Fe(III), means iron in an oxidation state of +3. The uncombined Fe(III) ion is simply Fe^{3+}.

Two of the most important bond formations for bioremediation, particularly of metals, are ionic and covalent. In ionic bonds, a complete transfer of electrons occurs from one atom to another. This creates two ions with opposing electric charge. The transfer is generally from a metal to a nonmetal. The metal loses one or more electrons and becomes a positive ion, a cation, and the nonmetal will receive the electron or electrons and become a negative ion, an anion. Most metals easily combine with oxygen to form metal oxides, and many ores consist of metal oxides. Oxygen in its ionic state has a valence of –2. Electrostatic attraction between the ions of opposite charge holds them together, creating a compound.

When atoms of two elements of about the same electronegativity react, they form bonds in which the electrons are shared about equally between atoms. Bonds formed by the sharing of electrons are covalent bonds. Covalent bonds between identical atoms (such as H_2) are nonpolar, or electrically uniform, whereas those between unlike atoms are polar, that is, one atom is slightly negatively charged and the other is slightly positively charged. This partial ionic character of covalent bonds increases with the difference in the electronegativities of the two atoms.

Oxidation–reduction, or "redox," is a chemical reaction in which there is either a complete transfer of electrons (creating an ionic bond), or a sharing of electrons with other atoms (creating a covalent bond). This changes the oxidation state of the atoms involved in the reaction. The atom that loses an electron is oxidized, and the atom that gains an electron is reduced. The distinction between ionic and covalent bonding is not absolute. Covalent bonds have a partially ionic character. Compounds often include both ionic and covalent bonds.

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1. To learn more about this topic, see *General Chemistry: Principles and Structure* (Brady, 1990).